

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Manfred Hesiler et al.

Group Art Unit: 1797

Examiner: David L. Sorkin

Serial No.: 10/802,455

Filed: March 17, 2004

For: PROCESS FOR THE CONTINUOUS PREPARATION OF
HIGH-VISCOSITY SILICONE COMPOSITIONS

Attorney Docket No.: WAS 0627 PUS

DECLARATION UNDER RULE 132

Commissioner for Patents
U.S. Patent & Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Dr. Johann Schuster, do hereby declare and state as follows:

1. I received my Diploma in Chemistry from the University of Regensburg in 1981, and my Dr. rer. nat. from that University in 1983. In 1984, I became employed by Wacker Chemie AG as a chemist in silicone rubber production, and from 1996 to 2000 I was appointed manager for global Silicone Rubber production. In 2000, continuing to the present, I have been Director of Technology for Silicone Elastomers, with global responsibility. I am the inventor of more than 20 patents and their worldwide patent families, directed to silicone rubber manufacturing. I am well acquainted with production methods used throughout the silicone rubber industry.

2. I am a coinventor of the subject matter disclosed and claimed in U.S. Application Serial No. 10/802,455, and am familiar with the content of the application, the Office Actions received from the United States Patent and Trademark Office, and the *Mathur*

and *Schuster* references cited by the Patent Examiner. I am the Johann Schuster of the *Schuster* patent, and am thus well qualified to discuss this reference, as well as the *Mathur* reference.

3. The claimed invention is directed to a continuous method of compounding filled, HTV silicone rubber compositions. In a first stage, the raw ingredients are intensively mixed in a kneading cascade. The compounded mixture thus produced is then fed to a reciprocating kneader. As a result of this method of preparation, the HTV rubber produced has a very low content of volatiles, and is remarkably free from color. These characteristics are highly important for HTV silicone rubbers. A low volatiles content is needed both for preventing escape of volatiles and/or formation of bubbles during the high temperature molding of the HTV rubbers, and to prevent the more volatile components from later blooming or forming an oily film on the surface of the cured part. Freedom from color causing impurities is associated with a high quality product, and also facilitates reliable and reproducible production of colored parts by incorporating pigments into the rubber, without any processing - induced coloration affecting the product color desired.

Continuous methods for producing HTV silicone rubber are known. However, these methods tend to produce HTV silicone rubber whose characteristics vary, and may suffer from inhomogeneity as well. Some of these methods generate significant amounts of color-causing impurities as well. An improved process for continuous production of HTV silicone rubber is disclosed in Achenbach et al. U.S. Patent 6,323,262, commonly assigned to Wacker Chemie AG. In the *Achenbach* patent, a variety of continuous mixers are disclosed, and a significant portion of the compounded product is fed back to the mixer inlet in order to produce an acceptable product. However, this recycle of a portion of the silicone rubber is technically complicated, and also reduces the product throughput which would otherwise be obtained without recycle. The product of this process has superior color as compared to other processes, but the color is still in need of improvement.

4. *Schuster* discloses a process for producing LSR (liquid silicone rubber), which is a product quite distinct from HTV silicone rubber. In the process disclosed in *Schuster*, a multi-chambered kneading cascade is used, and the silica filler is "treated" or "hydrophobic" silica. Hydrophilic silica, e.g. untreated fumed silica, is difficult to incorporate into either LSR or HTV compositions, since it has a very low density, approximately, 50g/l, while treated hydrophobic fillers have a much higher density, about 200 g/l. Hydrophilic silica is also difficult to incorporate due to the very hydrophobic silicone matrix. For these reasons, the *Schuster* patent does not disclose use of untreated filler, even though the organopolysiloxanes employed are liquids as opposed to plastic solids or gums.

5. Mathur U.S. Patent 6,548,574 discloses completely unrelated processes for preparing HTV silicone rubber. A problem with compounding HTV silicone rubber, whether by a batch process or a continuous process, is again directed to uniformly incorporating the filler. As discussed by *Mathur*, the prior method was to employ a treated silica and blend this filler with a high viscosity silicone gum to produce what *Mathur* calls a damp "treated premix." This damp premix was then compounded with further silicone. However, as *Mathur* notes, damp premix is difficult to handle and to meter into the process. Therefore, *Mathur* directs the skilled artisan not to use damp premix, but to instead intensively mix untreated filler and high viscosity silicone to form a dry, untreated premix. This untreated premix is then further compounded in a second stage with additional silicone rubber. The preparation of the untreated premix requires a mixer with exceptionally high shear, produced by rapidly moving blades. *Mathur* describes a Henschel mixer for batch processes and a continuous annular layer mixer if a continuous process is envisioned. Both these mixers are blade-type mixers with very high shearing action, which continuously "cuts and dices" the silicone rubber, while forcing filler into the small particles created.

6. One skilled in the art, reading *Mathur*, would not be motivated to replace the first mixer of *Mathur* with a kneading cascade. The Henschel and annular layer mixers of *Mathur* are both relatively high speed, blade type mixers, features which are necessary to

produce *Mathur's* dry premix. On the other hand, a kneading cascade has no cutting action because it contains no rotating blades. The rotors in the kneading cascade chambers revolve at relatively low speeds, at much lower levels of shear than a blade type mixer.


7. To illustrate the effect of a kneading cascade in the production of a filled intermediate product which *Mathur* terms an "untreated premix," Example 1 of *Schuster* was repeated, but with conventional hydrophilic filler (Wacker® HDK T30 silica) instead of *Schuster's* HDK SKS 300 hydrophobic silica. The hydrophilic silica is compacted badly, and up to chamber 6 of the kneading cascade is still in a powder phase. Tailback into the silica filler funnel occurred several times, since it was not possible to feed the bulky, low density silica as rapidly as necessary. The matrix discharged from the devolatilizing vessel was inhomogeneous and of very high viscosity. This mixture was incapable of being further processed. Therefore, no Shore A hardness, Mooney viscosity, or storage stability could be measured.

8. The same hydrophilic filler was also employed in a further example of the subject invention process. 60 Kg of HDK T30 hydrophilic silica was introduced into the kneading cascade in accordance with Example 1 of the present invention. The product exiting the reciprocating kneader was homogenous and exhibited good form stability. Its Mooney viscosity was 43 and the Shore A hardness of a cured part was 61. The product had low color and good storage stability.

9. In the claimed process, the ability to use an untreated filler in a first stage which is a kneading cascade is very surprising and unexpected. In preferred embodiments, the product exiting the kneading cascade is a homogenous, cohesive composition quite similar in appearance to the final HTV silicone rubber product. In contrast, the product exiting the *Mathur* mixer in his first stage is a dry powder, totally unlike HTV silicone rubber.

10. As one skilled in the art, I would not be motivated by *Mathur* to replace his high shear first stage mixer with a kneading cascade. Moreover, since *Schuster* requires a hydrophobic filler and *Mathur* requires an untreated, hydrophilic filler, these directly opposing teachings would, if anything, direct the skilled artisan away from the combination of *Mathur* and *Schuster* proposed by the Patent Examiner. Because of their diametrically opposed teachings relative to the type of filler, as well as because *Schuster* is directed to LSR and not HTV rubber, it is apparent that these references cannot even be physically combined. Each reference teaches doing what the other reference teaches not to do.

I hereby declare that all statements made herein of our knowledge are true and that all statements made on information and belief are believed to be true; and further that the statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statement may jeopardize the validity of the application or any patent issuing thereon.



Dr. Johann Schuster

Date: 8.5.2009

1.Stufe: „Conterna“, 6 Kammern je 10l Volumen, Gesamtdurchsatz 200kg/h

In die Kammer 1 wird das Polymer eindosiert (120kg/h), zudem der Weichmacher (20kg/h), in die Kammer 2 der Füllstoff (60kg/h). Der Gesamtdurchsatz betrug folglich ca. 200kg/h. Die Drehzahlen in den Kammern 1-4 liegen bei 35 UpM. An Hand der Leistungsaufnahme der Einzelantriebe der Kammern kann registriert werden, dass in der 2. Und 3. Knetkammer wohl eine brockige Konsistenz der Masse vorliegt. In der 4.Knetkammer ist die Leistungsaufnahme ruhiger und höher, hier liegt eine homogene zusammenhängende Masse vor. Kammer 1 - 4 wurden mit 50Upm betrieben. In den Kammern 5 und 6 wird mit 40 UpM nachgeknetet und gleichzeitig erfolgt aus Kammer 6 der Produktaustrag. Die 6 Kammern werden nicht gekühlt und nicht geheizt, die Temperaturen ziehen von ca. 45°C in der 1. Stufe auf ca. 150°C in der 6. Kammer an.

Ohne Zwischenlagerung wird der Kautschuk einem Bussknetter vom Typ LR100 zugeführt. Da beide Anlagenteile in ihrer Dimensionierung nicht aufeinander abgestimmt sind, mussten der Produktstrom im Verhältnis 120:80 geteilt werden. Hierzu benutzten wir eine Breitschlitzdüse, die den Produktstrom über einen eingeschweißten Steg in den gewünschten Massenstrom teilt. 80kg/h werden ausgeschleust (**=Probe 1, nicht erfindungsgemäß**). Die restlichen 120kg/h Kautschuk werden in den oben erwähnten Bussknetter dosiert und der 2.erfindungsgemäße Verfahrensschritt wird verifiziert.

2.Stufe: „Busckneter LR100“

Der uns zur Verfügung stehende Busckneter vom Typ LR100 gliedert sich in 5 Zonen (Schüsse) mit folgendem Aufbau: 1.Zone 3D, 2. – 5.Zone jeweils 4D. Alle Zonen sind über Stauringe voneinander getrennt. Mit Hilfe einer Vakuum-Wasserringpumpe beaufschlagten wir die Zonen 2 – 5 mit einem Vakuum in Höhe von 100mbar(abs.). Die Temperierung der einzelnen Schüsse und der Welle des Busckneters wählten wir so, daß sich beginnend ab dem 2.Schuss bei einer Wellendrehzahl von 150 UpM eine Produkttemperatur längs des Kneters von ca. 180 -200°C einstellte. Der über die Conterna produzierte Kautschuk mit einem Massenstrom von ca. 120kg/h wird in die Zone 1 des Busckneters mit einer Produkttemperatur von ca. 150°C dosiert. In den Zonen 2 – 5 wird er intensiv geknetet und dabei flüchtige Bestandteile der Kautschukmasse optimal entfernt. Über eine gekühlte Austragsschnecke wird der Kautschuk ausgetragen und kann als **erfindungsgemäße Probe 2** untersucht werden.

Als Vergleichsbeispiele dienen das Beispiel 1(erfindungsgemäß) und Beispiel 3(nicht erfindungsgemäß =WA9035) in WA9850. Die dort aufgeführten Versuche wurden wiederholt, die Kautschukproben wie folgt bezeichnet: Beispiel 1 = **Probe 3 (nicht erfindungsgemäß)**, Beispiel 3 = **Probe 4 (nicht erfindungsgemäß)**

Prüfung der hergestellten Siliconkautschukmassen

-Die Proben 1 – 4 wurden von uns hinsichtlich ihrer **Lagerstabilität** über einen Zeitraum von 3 Monaten beurteilt, also Messungen der Mooney-Viskosität in definierten Zeitintervallen, Beurteilung des Verhaltens auf dem Walzwerk. In der Tabelle ist nur die qualitative Probenbeurteilung nach 3 Monaten aufgeführt.

-Am Rohkautschuk wurde ferner die **Flüchtigkeit** bei 200°C gemessen.
Bedingungen: 1g Kautschuk/4h/200°C , Angabe in %Flüchtige.

Der Kautschuk wurde

- a)-mit 0,7%Dicumylperoxid(=Vernetzer C1) 15 Minuten bei 165°C und
- b)-mit 1,5%Di(2,4-)Dichlorobenzoyl)peroxide(50%ig)(=Vernetzer E) 10 Minuten bei 135°C

in einer beheizten Presse zwischen Platten vulkanisiert. Die Vulkanisate anschließend im Umlufschrank 4h bei 200°C getempert, danach das Aussehen dieser Vulkanisate beurteilt, also den Grad der **Verfärbung**.

1= nicht verfärbt, 4= stark verfärbt

Probe	Lagerstabilität	Flüchtigkeit	Verfärbung Vulkanisate	
			Vern. E	Vern. C1
1	mittel	1,9%	3	4
2	gut	0,5%	1	1 – 2
3	gut	1,4%	1 - 2	2 - 3
4	schlecht	1,3%	1 - 2	2 - 3